

Theory of phase transformation and reorientation in single crystalline shape memory alloys

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Abstract

A constitutive model, based on an $(n + 1)$ -phase mixture of the Mori–Tanaka average theory, has been developed for stress-induced martensitic transformation and reorientation in single crystalline shape memory alloys. Volume fractions of different martensite lattice correspondence variants are chosen as internal variables to describe microstructural evolution. Macroscopic Gibbs free energy for the phase transformation is derived with thermodynamics principles and the ensemble average method of micro-mechanics. The critical condition and the evolution equation are proposed for both the phase transition and reorientation. This model can also simulate interior hysteresis loops during loading/unloading by switching the critical driving forces when an opposite transition takes place.

1. Introduction

Shape memory alloys have been recognized as promising materials for various applications for decades [1, 2]. More recently, they have also found applications as micro-actuator devices in MEMS [2–5]. The mechanism behind the unique shape memory phenomenon is the diffusionless phase transformation between the high-temperature stable phase austenite and low-temperature stable phase martensite, and reorientation among martensite variants. Modeling mechanical and microstructural behaviors of shape memory alloys is considerably complex due to the nonlinear behavior and the presence of hysteresis. Furthermore, those behaviors are temperature dependent in many cases.

In view of engineering applications, multidimensional constitutive models have been developed recently; see, for instance, [6–19]. Most previous models adopted a statistical strategy ranging from the microscale, through the mesoscale to the macroscale. However, confusion with regard to the fundamentals of micromechanical models still exists, largely

due to the complexity in microstructure during the martensitic transformation. Those fundamental concepts are critical to understanding the mechanism of martensitic transformation. To name a few:

- (1) What are the potential wells of martensitic transformation; habit plane variants (HPVs) or lattice correspondence variants (LCVs), or both?
- (2) How can one model the interaction energy between martensite and austenite, and among martensite variants?
- (3) What is the mechanism of forming an interior hysteresis loop, and how does one model it?

These three aspects of martensitic transformation are further reviewed as follows.

Lattice correspondence variant and habit plane variant. The phenomenological theory of martensite crystallography [20–23] has been successfully applied in investigating the microstructure evolution of the martensite/austenite inter-phase and martensite twins. This theory allows continuous

macro-displacement with heterogeneous microscopic deformation. Hence, the Hadamard jump condition becomes an internal geometric restraint, which requires the interface between the martensite lattice correspondence variants to be a twin plane and that between austenite and martensite to be a habit plane [24, 25]. It is noted that habit plane variants are not always the elementary units that compose the bulk martensite. Instead they are often formed by even smaller single crystalline units, which have a unique lattice correspondence with austenite [26]. In this paper, we use ‘habit plane variant’ to describe the morphological change of forward and reverse transformations between austenite and martensite, while employing ‘lattice correspondence variant’ to specify martensite lattice correspondence during the reorientation process. Since the order of symmetry of martensite is lower than that of austenite, n lattice correspondence variants may be induced from one austenite crystal after martensitic phase transformation. In some shape memory alloys (e.g., CuZnGa and CuZnAl, which involve DO₃ austenite and 18R martensite) [27], the habit plane variant is a martensite lattice correspondence variant. In other shape memory alloy transformations, such as the DO₃ austenite to 2H martensite transformation in CuAlNi [28–31], and B2 austenite to B19’ martensite transformation in TiNi [32], the habit plane variant includes two twin-related lattice correspondence variants. Figure 1 is a sketch of a habit plane variant which consists of a pair of twinned lattice correspondence variants. Assuming \mathbf{U}_i is the right stretch tensor of Bain strain in lattice correspondence variant i , the deformations in the two lattice correspondence variants i and j are \mathbf{U}_i and \mathbf{U}_j , respectively. Thus, the deformation of a habit plane variant may be expressed as $\kappa\mathbf{U}_j + (1 - \kappa)\mathbf{R}\mathbf{U}_i$, where \mathbf{R} is the rotation of variant i with regard to variant j . The volume fraction ratio between the twinned lattice correspondence variants κ is a constant, as determined by the lattice parameters of austenite and martensite. In the case of CuAlNi, the type II twin habit plane variant has one lattice correspondence variant of 0.3007 and another of $(1 - 0.3007)$ [28, 29].

Continuum thermoelasticity, developed by Ericksen [33], Ball and James [24] and others, studies the atomic displacement and macroscopic deformation in crystalline solids undergoing a martensitic transformation. It uses the Cauchy–Born hypothesis, where minimum total free energy is required for any mechanical response. The total free energy usually comprises deformation energy (or elastic strain energy) and loading device energy (refer to equation (13) in [34], and equation (8) in [35]). The deformation energy is assumed to be a smooth function of temperature and deformation gradient. It must be frame independent and reaches its minimum at the bottom of the potential well. According to continuum thermoelasticity, each lattice correspondence variant is a potential well. The system would have $n + 1$ potential wells (n lattice correspondence variants for martensite plus one for austenite). Thus, the deformation energy is minimized if the total strain equals the eigenstrain of each martensite lattice correspondence variant (without elastic strain) or zero (corresponding to austenite). It is well known that in forward transformation austenite is much easier to transform into habit plane variants than lattice correspondence variants. In order

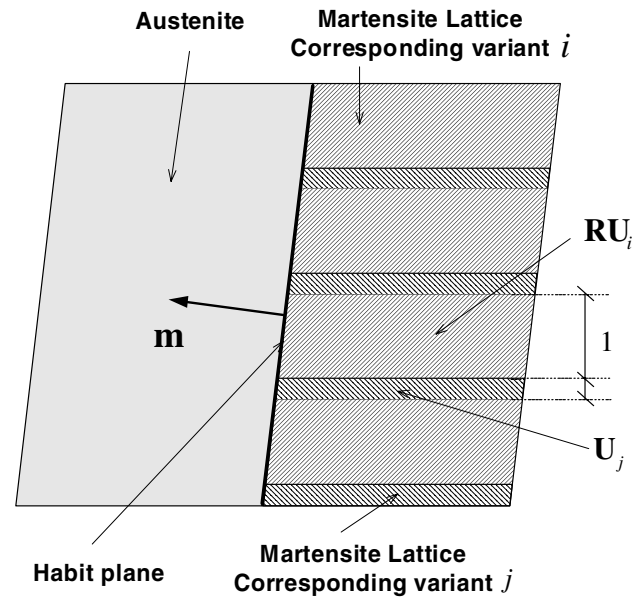


Figure 1. A habit plane variant consists of a pair of twinned lattice correspondence variants.

to obtain thermodynamic forces corresponding to habit plane variants, some previous models simply chose habit plane variants (or lattice correspondence pairs) as potential wells. It should be pointed out that a habit plane variant does not always correspond to an energy potential well. In order to establish the kinetic mechanism of martensitic transformation, the relationship between the martensite lattice correspondence variant and habit plane variant has to be identified. It is obvious that if the habit plane variants are chosen as potential wells, martensite reorientation cannot be properly described, since reorientation happens among lattice correspondence variants, which are subunits of habit plane variants. A particular example is discussed in [34]. In some of the previous models [12, 36–39], lattice correspondence variants are chosen as potential wells instead of habit plane variants. These models use a transformation ‘yield’ surface [40] to simulate the phase transformation process, rather than proposing thermodynamic driving forces for martensite habit plane variants. In the present paper, we demonstrate that lattice correspondence variants should be chosen as potential wells. Thermodynamic driving forces corresponding to martensite habit plane variants can still be explicitly derived out under this framework. Further, thermodynamic models for forward/reverse transformations between austenite and martensite, and reorientation among martensite variants, have been developed using this protocol.

Interaction energy. Determination of the overall deformation energy is critical in modeling the transition in shape memory alloys. Although continuum thermoelasticity has outlined the main characteristics of deformation energy (e.g. potential wells, frame independence, and smoothness of deformation gradient and temperature) and the upper bound and lower bound of deformation energy have been discussed previously [38, 41], no explicit formula for the deformation energy has been proposed. In practice, Hooke’s law, linking the deformation energy with the local elastic deformation,

applies reasonably accurately in the close vicinity of a local well [42]. We recently combined Hooke's law with the volume average scheme and suggested that the macroscopic deformation energy can be divided into two parts: the energy induced by macroscopic external stress and internal interaction energy [43]. Internal interaction energy is generated by the inhomogeneous phase transformation eigenstrain and it does not depend on the external (macroscopic) stress. Therefore, the only issue remaining is how to determine the internal interaction energy.

Previously, martensite variants have been considered as inclusions within an austenite medium and the interaction energy of a multicomponent system is estimated by Eshelby's inclusion theory. Eshelby's inclusion theory is only valid for one ellipsoidal inclusion embedded within an infinite matrix; it may not be accurate for a multi-inclusion case. Martensite/austenite interface and interface among martensite variants are planes; martensite must be in polyhedral shape rather than ellipsoid. Furthermore, inclusion theory is not applicable for the phase transformation in single crystalline shape memory alloys, in which case an austenite single crystal transforms into one martensite variant upon loading. The internal interaction energy of a multicomponent mixture can be derived by the interface operator technique [14, 44]. In Siredey's work, grains are divided into a series of domains. Each domain is assumed to end at a grain boundary and a domain meets others on one side only. By definition, only one type of martensite habit plane variant is assigned for each domain. The internal stress caused by incompatible deformation in each domain is assumed to be constant. Subsequently, a second-order polynomial function in terms of volume fractions of martensite habit plane variants can be obtained. Coefficients of this polynomial are determined by the interfacial operator. Hence, they are dependent upon the microstructure of a particular shape memory alloy, and can be determined at a microscopic level.

Mori and Tanaka [45] have proven that if two phases are mixed together in a random and uniform fashion, the interaction energy produced by the incompatible deformation is proportional to $z(1 - z)$ [46]. Here z is the volume fraction of one phase. Similar formulae have been used for shape memory alloys [47–51]. Unfortunately, this simple closed-form solution is only for two-phase mixtures. In shape memory alloys, there are n martensite variants plus one for austenite. Thus, the interaction energy in an $(n + 1)$ component mixture has to be considered. We recently extended the Mori–Tanaka theory to an $(n + 1)$ -component mixture [43]. It can subsequently be concluded that the inclusion theory is only applicable for one ellipsoidal inclusion case, while Mori–Tanaka theory is valid for the multi-inclusion case. The volume fraction of martensite has to be much less than 1 in the inclusion theory, while it can be any value between 0 and 1 in Mori–Tanaka theory. It is noted that the interaction energy of a two-component mixture estimated by the inclusion theory also appears as a second-order polynomial. But this is quite different from that predicted by Mori–Tanaka theory. The coefficient is determined by an Eshelby tensor in the former, while the calibration can be done by a macroscale experiment

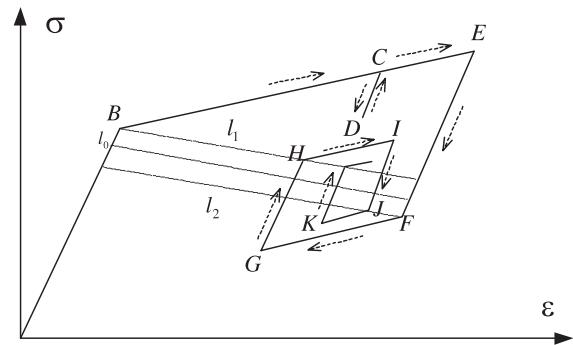


Figure 2. Sketch of an interior hysteresis loop.

in the latter. In addition, it has been proven that the total number of independent constants in the interaction energy is no more than the number of martensite lattice correspondence variants [43].

Interior hysteresis loop. A complex interior hysteresis loop was observed in uniaxial tensile tests in single crystalline shape memory alloys [47–53], and a similar phenomenon has been reported in martensite reorientation between two martensite lattice correspondence variants [34]. These interior hysteresis loops were given various names, such as internal elasticity, internal yield and internal recovery in the literature (for example figure 2 in [48], figures 1 and 4 in [49], figures 4, 5 and 8 in [50]). Considering an isothermal loading/unloading process as shown in figure 2, phase transformation starts at B upon loading. If unloading at C, it moves from C to D. During reloading from D, it returns to C elastically. As there is no reverse phase transformation upon unloading, the last transformation state in the forward transition at point C is remembered. The forward transition will not restart until reloading to C. If unloading from point E, a reverse transition appears ($E \rightarrow F \rightarrow G$ as shown in figure 2); the last transformation state in the forward transition at point E is obliterated. During reloading from G, the forward transformation restarts at H. A similar phenomenon happens in the reverse transformation and reorientation (e.g., tension/compression cycling). *Oblivion* plays an important role in the formation of an interior hysteresis loop, which happens when an internal state crosses lines l_1 and l_2 in figure 2. Huo and Müller [50] concluded that the interior hysteresis loop is due to history-dependent pseudoelasticity, and the fraction of the last transformation state is remembered. Fedelich and Zanzotto [48] suggested choosing the fraction of martensite variant in the last transformation as an additional internal variable to describe these loops. The present paper only deals with transformations with a stable hysteresis loop; refer to [54, 55] for the instability of the phase transformation.

We aim at developing a robust micro-mechanical model to address the above three issues in this paper. In section 2, the macroscopic Gibbs free energy is expressed as a function of volume fractions of different martensite lattice correspondence variants. Basic transition processes (e.g. forward/reverse transformations and reorientation) and the transition law, and the prediction of an interior hysteresis loop are investigated in section 3. Conclusions and outlook of the proposed

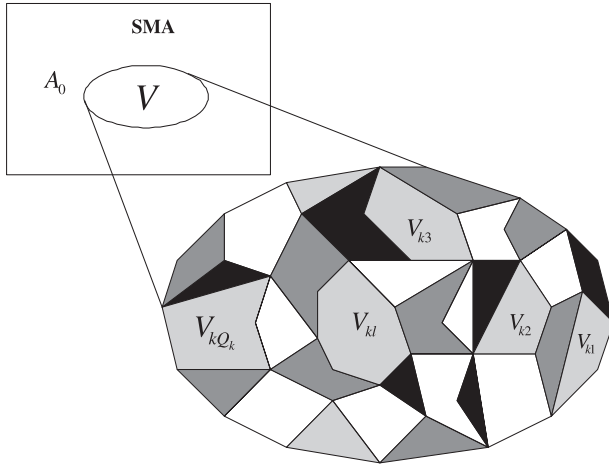


Figure 3. Sketch of a representative volume element. Areas with different shades stand for different martensite lattice correspondence variants. $k = 0, 1, 2, \dots, n, l = 1, 2, \dots, Q_k$.

thermodynamic models for shape memory alloys are given in section 4.

2. Thermodynamics of martensitic transformation

In this section, the non-equilibrium thermodynamics of martensitic transformation is investigated using the ensemble average method. Martensite lattice correspondence variants are chosen as internal variables to describe the microstructural configuration. Potential differences between the martensite lattice correspondence variant and austenite are derived from macroscopic Gibbs free energy.

A single crystalline shape memory alloy is pure austenite if the material is stress-free and the temperature is higher than its austenite finish temperature. Taking a representative volume element (with volume V and its boundary A_0) from a single crystal, a martensitic transformation may be induced by either stressing or cooling (figure 3). In both cases, the microstructural evolution is by means of the growth of martensite at the expense of austenite until, ideally, no more austenite exists.

Within martensite, there are n possible lattice correspondence variants. Therefore, in a representative volume element, $n + 1$ components may coexist (let $k = 1, 2, \dots, n$ represent n martensite lattice correspondence variants, and $k = 0$ for austenite). As shown in figure 3, one martensite lattice correspondence variant may be found inside many different regions in the representative volume element. The same martensite lattice correspondence variants are represented by the same shade in figure 3. We assume that the number of regions with a particular type of martensite lattice correspondence variant k is Q_k and the volume of the l th ($l = 1, 2, \dots, Q_k$) region with martensite lattice correspondence variant of type k is V_{kl} (with boundary A_{kl}). For consistency, all vectors and tensors are in bold face and the summation convention for repeated indices is not used in this paper. For simplicity, we only consider elastic deformation and deformation due to the phase transformation; and we assume that the two phases (martensite and austenite)

share the same thermal and physical properties. Thus the following assumptions are made:

- (1) The total deformation can be divided into two parts: namely, the elastic deformation and deformation induced by the transformation.
- (2) The elastic modulus (\mathbf{L}) of austenite is the same as that of martensite. The elastic compliance tensor is given by $\mathbf{M} = \mathbf{L}^{-1}$.
- (3) The specific heat C_V and heat conduction coefficient k_0 of austenite and martensite are the same.
- (4) Martensite in three-dimensional space is randomly and uniformly distributed.
- (5) The density ρ , temperature field T , heat flow \mathbf{q} and specific heat source \dot{r} are uniform in the representative volume element. Only macroscopic heat conduction is considered and the heat conduction among different phases within the representative volume element is ignored.
- (6) Thermal expansion is ignored.

According to assumption 1, the total strain \mathbf{e}_{kl} is the sum of elastic strain and phase transition strain:

$$\mathbf{e}_{kl} = \mathbf{e}_{kl}^e + \mathbf{E}_k^{\text{tr}} \quad (l = 1, 2, \dots, Q_k) \quad (1)$$

where \mathbf{e}_{kl}^e is the elastic strain and \mathbf{E}_k^{tr} is the eigenstrain due to the phase transformation from austenite to type k martensite lattice correspondence variant. It is noticed that, for V_{kl} ($l = 1, 2, \dots, Q_k$), which corresponds to the same variant of type k located at various places, their phase transformation eigenstrains are the same although their elastic strain \mathbf{e}_{kl}^e may be different.

If the point group of austenite is given by \mathbb{P}_a and that of martensite is \mathbb{P}_m , then \mathbb{P}_m is a subgroup of \mathbb{P}_a [43]. Let \mathbb{L} be the left coset of \mathbb{P}_m in \mathbb{P}_a , i.e.,

$$\mathbb{P}_a = \mathbb{L} \otimes \mathbb{P}_m. \quad (2)$$

We have

$$\mathbf{E}_k^{\text{tr}} = \mathbf{R}_k \mathbf{E}_1^{\text{tr}} \mathbf{R}_k^T, \quad \mathbf{R}_k \in \mathbb{L}, \quad (3)$$

where $k = 1, 2, 3, \dots, n$, and n is the total number of lattice correspondence variants. For austenite ($k = 0$), there is no phase transformation term but elastic deformation only, i.e.,

$$\mathbf{e}_{0l} = \mathbf{e}_{0l}^e \quad (l = 1, 2, \dots, Q_0). \quad (4)$$

Assuming that the specific internal energies and specific entropies of austenite and martensite at the reference temperature T_0 are u_0^A, u_0^M, h_0^A , and h_0^M , respectively, then the specific entropy η^M , elastic energy ϕ_{kl} , and specific internal energy u_{kl} for martensite V_{kl} ($k \neq 0$) may be expressed as

$$\rho \eta^M(T) = h_0^M + C_V \ln \left(\frac{T}{T_0} \right) \quad (k \neq 0), \quad (5)$$

$$\phi_{kl} = \frac{1}{2} (\mathbf{e}_{kl} - \mathbf{E}_k^{\text{tr}}) : \mathbf{L} : (\mathbf{e}_{kl} - \mathbf{E}_k^{\text{tr}}) = \frac{1}{2} \boldsymbol{\sigma}_{kl} : \mathbf{M} : \boldsymbol{\sigma}_{kl}, \quad (6)$$

$$\rho u_{kl} = u_0^M + C_V (T - T_0) + \phi_{kl} \quad (k \neq 0), \quad (7)$$

where $l = 1, 2, \dots, Q_k$ and $\boldsymbol{\sigma}_{kl}$ is the stress applied on the martensite volume specified by kl . For austenite V_{0l} ($k = 0$),

the specific entropy η^A , elastic energy ϕ_{0l} , and specific internal energy u_{0l} are

$$\rho\eta^A(T) = h_0^A + C_V \ln\left(\frac{T}{T_0}\right) \quad (k=0), \quad (8)$$

$$\phi_{0l} = \frac{1}{2}\mathbf{e}_{0l} : \mathbf{L} : \mathbf{e}_{0l} = \frac{1}{2}\boldsymbol{\sigma}_{0l} : \mathbf{M} : \boldsymbol{\sigma}_{0l}, \quad (9)$$

$$\rho u_{0l} = u_0^A + C_V(T - T_0) + \phi_{0l}, \quad (10)$$

where $l = 1, 2, \dots, Q_0$. Hence, $\mathbf{e}_{kl} = \mathbf{E}_k^{\text{tr}}$ ($k = 1, 2, \dots, n$) and $\mathbf{e}_{0l} = 0$ form $n + 1$ potential wells.

For any given microscopic quantity ψ , define its corresponding macroscopic average as

$$\langle \psi \rangle = \frac{1}{\rho V} \iiint_V \rho \psi \, dV = \frac{1}{\rho V} \sum_{k=0}^n \sum_{l=1}^{Q_k} \iiint_{V_{kl}} \rho \psi_{kl} \, dV, \quad (11)$$

where ρ is the macroscopic density of the representative volume element. Recalling assumption (4), one has

$$\langle \psi \rangle = \frac{1}{V} \iiint_V \psi \, dV = \frac{1}{V} \sum_{k=0}^n \sum_{l=1}^{Q_k} \iiint_{V_{kl}} \psi_{kl} \, dV. \quad (12)$$

Let the volume fraction of type k lattice correspondence variant in a representative volume element be

$$z_k = \frac{V_k}{V}, \quad (13)$$

where

$$V_k = \sum_{l=1}^{Q_k} V_{kl}. \quad (14)$$

Obviously,

$$\sum_{k=0}^n z_k \equiv 1. \quad (15)$$

The macroscopic volume average strain (i.e. in equation (11) $\psi = \mathbf{e}$) may be defined by [56, 57]

$$\mathbf{E} = \langle \mathbf{e} \rangle = \frac{1}{V} \sum_{k=0}^n \sum_{l=1}^{Q_k} \iiint_{V_{kl}} \mathbf{e}_{kl} \, dV \quad (16)$$

where \mathbf{e} is the microscopic strain; thus

$$\mathbf{E} = \mathbf{E}^e + \mathbf{E}^{\text{tr}}, \quad (17)$$

where \mathbf{E}^e and \mathbf{E}^{tr} are the macroscopic elastic strain and macroscopic phase transformation strain, respectively, and

$$\mathbf{E}^e = \langle \mathbf{e}^e \rangle = \frac{1}{V} \sum_{k=0}^n \sum_{l=1}^{Q_k} \iiint_{V_{kl}} \mathbf{e}_{kl}^e \, dV, \quad (18)$$

$$\mathbf{E}^{\text{tr}} = \sum_{k=1}^n z_k \mathbf{E}_k^{\text{tr}} \quad (19)$$

where \mathbf{e}^e is the microscopic elastic strain. Similarly, the macroscopic average of specific entropy ξ , elastic energy Φ and specific internal energy U can be defined as

$$\xi = \langle \eta \rangle, \quad (20)$$

$$\Phi = \langle \phi \rangle, \quad (21)$$

$$U = \langle u \rangle. \quad (22)$$

Substituting equations (5)–(10) into (20)–(22), and referring to equation (21), one has

$$\begin{aligned} \rho\xi = \langle \rho\eta \rangle &= z_0 \left[h_0^A + C_V \ln\left(\frac{T}{T_0}\right) \right] \\ &+ \sum_{k=1}^n z_k \left[h_0^M + C_V \ln\left(\frac{T}{T_0}\right) \right], \end{aligned} \quad (23)$$

$$\begin{aligned} \rho U = \langle \rho u \rangle &= z_0 [u_0^A + C_V(T - T_0)] \\ &+ \sum_{k=1}^n z_k [u_0^M + C_V(T - T_0)] + \Phi. \end{aligned} \quad (24)$$

Supposing that the macroscopic stress applied on volume V is $\boldsymbol{\Sigma}$, it is the conjugate stress with macroscopic strain \mathbf{E} [56–59], which has to satisfy

$$\frac{1}{V} \iiint_V \boldsymbol{\sigma} : \dot{\mathbf{e}} \, dV = \boldsymbol{\Sigma} : \dot{\mathbf{E}}. \quad (25)$$

It would be convenient to define all stress and strain tensors in a reference configuration, say the $\boldsymbol{\sigma}$ (or $\boldsymbol{\Sigma}$) second Piola–Kirchhoff stress tensor (or Lagrangian Piola–Kirchhoff stress) and the \mathbf{e} (or \mathbf{E}) Lagrangian strain tensor. According to [43], the total macroscopic deformation energy is a sum of macro-elastic energy in the absence of transformation and the internal interaction energy due to martensitic transformation in the absence of external stress, that is

$$\Phi = \frac{1}{2} \boldsymbol{\Sigma} : \mathbf{M} : \boldsymbol{\Sigma} + f^s, \quad (26)$$

where f^s is the ‘stored elastic energy’—internal energy due to the internal stress field $\boldsymbol{\sigma}_{\text{int}}$ (induced by eigenstrain $\boldsymbol{\varepsilon}^*$).

$$f^s = \Phi_{\text{int}} = -\frac{1}{2V} \iiint_V \boldsymbol{\sigma}_{\text{int}} : \boldsymbol{\varepsilon}^* \, dV \quad (27)$$

and

$$\boldsymbol{\varepsilon}^* = \begin{cases} \mathbf{E}_k^{\text{tr}} & \text{if } \mathbf{x} \in V_{kl} \\ 0 & \text{if } \mathbf{x} \in V - \Omega, \end{cases} \quad (28)$$

is the microscopic eigenstrain of the phase transformation; Ω denotes the total volume occupied by martensite.

It has been proved that f^s does not directly depend upon the external stress field; it is a second-order polynomial function of martensite lattice correspondence variant fractions [43], i.e.,

$$f^s = \Phi_{\text{int}} = A z_0 (1 - z_0) + \frac{1}{2} \sum_{k=1}^n \sum_{\substack{l=1 \\ l \neq k}}^n B_{kl} z_k z_l, \quad (29)$$

where A and B_{kl} are material constants describing the interaction between austenite and martensite and among martensite variants, respectively. A and B_{kl} should be calibrated experimentally at macroscopic scales. It was also proved that the maximum total number of independent B_{kl} is $n - 1$ [43]. Substituting equation (26) into (24) results in

$$\begin{aligned} \rho U &= \frac{1}{2} \boldsymbol{\Sigma} : \mathbf{M} : \boldsymbol{\Sigma} + z_0 [u_0^A + C_V(T - T_0)] \\ &+ \sum_{k=1}^n z_k [u_0^M + C_V(T - T_0)] + f^s. \end{aligned} \quad (30)$$

The total work includes work done by the surface force and the body force, respectively. We define the total work rate per unit volume as

$$\dot{W} = \frac{1}{V} \left[\int \int_{A_0} \boldsymbol{\sigma} : (\mathbf{v} \otimes \mathbf{n}) dA + \int \int \int_V \mathbf{f} \cdot \mathbf{v} dV \right], \quad (31)$$

where \mathbf{v} is the velocity, \mathbf{n} is the outwards normal direction of boundary A_0 , and \mathbf{f} is the body force. Note the equilibrium of an object subjected to an external stress and body force:

$$\frac{\partial \boldsymbol{\sigma}}{\partial \mathbf{x}} + \mathbf{f} = 0. \quad (32)$$

Referring to equation (25), equation (31) can be rewritten as

$$\dot{W} = \frac{1}{V} \int \int \int_V \boldsymbol{\sigma} : \dot{\mathbf{e}} dV = \boldsymbol{\Sigma} : \dot{\mathbf{E}}. \quad (33)$$

One may choose $(\boldsymbol{\Sigma}, z_k, T)$ as independent variables at the macroscopic scale. The macroscopic Gibbs free energy function is defined by

$$\rho G = \rho U - T\rho\xi - \boldsymbol{\Sigma} : \mathbf{E}. \quad (34)$$

By substituting equations (17), (19), (23), and (30) into (34), we obtain that

$$\begin{aligned} \rho G &= \rho U - T\rho\xi - \boldsymbol{\Sigma} : \left(\mathbf{E}^c + \sum_{k=0}^n z_k \mathbf{E}_k^{\text{tr}} \right) \\ &= \rho U - T\rho\xi - \boldsymbol{\Sigma} : \mathbf{M} : \boldsymbol{\Sigma} - \boldsymbol{\Sigma} : \left(\sum_{k=0}^n z_k \mathbf{E}_k^{\text{tr}} \right) \\ &= z_0 [u_0^A + C_V(T - T_0)] + \sum_{k=1}^n z_k [u_0^M + C_V(T - T_0)] \\ &\quad + f^s - T \left\{ z_0 \left[h_0^A + C_V \ln \left(\frac{T}{T_0} \right) \right] \right. \\ &\quad \left. + \sum_{k=1}^n z_k \left[h_0^M + C_V \ln \left(\frac{T}{T_0} \right) \right] \right\} \\ &\quad - \boldsymbol{\Sigma} : \left(\sum_{k=0}^n z_k \mathbf{E}_k^{\text{tr}} \right) - \frac{1}{2} \boldsymbol{\Sigma} : \mathbf{M} : \boldsymbol{\Sigma}. \end{aligned} \quad (35)$$

From equation (35), we get

$$\mathbf{E} = -\rho \frac{\partial G}{\partial \boldsymbol{\Sigma}} = \mathbf{M} : \boldsymbol{\Sigma} + \sum_{k=0}^n z_k \mathbf{E}_k^{\text{tr}} \quad (36)$$

and

$$\xi = -\frac{\partial G}{\partial T}. \quad (37)$$

Let Ξ_k be potential difference between type k martensite lattice correspondence variant and austenite, then

$$\Xi_k = -\rho \frac{\partial G}{\partial z_k} = \boldsymbol{\Sigma} : \mathbf{E}_k^{\text{tr}} + (\Delta h T - \Delta u) - \frac{\partial f^s}{\partial z_k}, \quad (38)$$

where

$$\begin{aligned} \Delta h &= h_0^M - h_0^A \\ \Delta u &= u_0^M - u_0^A. \end{aligned} \quad (39)$$

The phase equilibrium temperature is determined by $T^{\text{eq}} = \frac{\Delta u}{\Delta h}$.

Letting $\rho T \eta^*$ be the total entropy product in representative volume element (V), which includes contributions from phase transformation and heat conduct, the second thermodynamic principle may be written as

$$\rho T \eta^* = \sum_{k=1}^n \Xi_k \dot{z}_k - \frac{1}{T} \mathbf{q} \cdot \nabla T \geq 0. \quad (40)$$

3. Transition process

In this section, we use progress variables and stoichiometric coefficients to describe the transition process in shape memory alloys. The thermodynamic driving force for an individual progress variable is obtained. Critical conditions and evolution equations for the forward transformation, reverse transformation and reorientation are derived.

3.1. Basic transition process

In section 2, we have defined and derived potentials for each martensite lattice correspondence variant and austenite. However, austenite and martensite lattice correspondence variants may simultaneously vary their volume fractions in a real transition process. For instance, upon cooling in a piece of stress-free austenite shape memory alloy, all martensite habit plane variants may be produced equally and grow simultaneously at a critical temperature (also called *self-accommodation* martensite). For a simplest transition process, the phase transformation starts with austenite transforming into a habit plane variant, which may include two lattice correspondence variants in some shape memory alloys. On the other hand, reorientation is a transition process between two martensite lattice correspondence variants.

In a given transition process (denoted by subscript l), the volume fractions of austenite and each martensite lattice correspondence variant vary proportionally. The rate among these variations may be described in terms of stoichiometric coefficients ($v_{0l}, v_{1l}, v_{2l}, \dots, v_{nl}$). Mass conservation yields

$$\sum_{k=0}^n v_{kl} = 0. \quad (41)$$

The progress state of the process may be presented by a progress variable ζ_l . It varies between 0 and 1, where $\zeta_l = 0$ is for the beginning of a process and $\zeta_l = 1$ when the process finishes. Thus, the variations of volume fractions of austenite and each martensite lattice correspondence variant due to this transition process can be expressed by

$$\dot{z}_k = v_{kl} \dot{\zeta}_l \quad (k = 0, 1, 2, \dots, n). \quad (42)$$

From equation (42), the total potential variation rate of martensite takes the form of

$$\sum_{k=1}^n \Xi_k \dot{z}_k = \left[\sum_{k=1}^n \Xi_k v_{kl} \right] \dot{\zeta}_l = \Pi_l \dot{\zeta}_l, \quad (43)$$

where

$$\Pi_l = \sum_{k=1}^n \Xi_k v_{kl}. \quad (44)$$

This is the thermodynamic driving force for a specific progress variable ζ_l . Equation (44) shows that the thermodynamic driving force of any transition process is a linear combination of thermodynamic driving forces of lattice correspondence variants. The combination coefficient is the stoichiometric coefficient of the transition process.

Any complex transition process can be considered as a combination of these basic processes, namely, forward transformation, reverse transformation and reorientation. In the case where the habit plane variant is the lattice correspondence variant, the stoichiometric coefficient of the forward phase transformation (from austenite to type l martensite lattice correspondence variant) is

$$\begin{array}{ccc} \text{element 0} & \text{element } l \\ \Downarrow & \Downarrow \\ (v_{0l}, v_{1l}, v_{2l}, \dots, v_{nl}) & = (-1, 0, \dots, 0, 1, 0, \dots, 0). \end{array} \quad (45)$$

The first element in the right-hand side of equation (45) is -1 , the l th element is $+1$, and all other columns are 0. Substitution of equation (45) into (44) yields

$$\Pi_l = \Xi_l. \quad (46)$$

If the habit plane variant is not a subunit of martensite, it has to be composed of a pair of twinned martensite lattice correspondence variants. Under this condition, in a forward phase transformation austenite transforms into two twinned martensite lattice correspondences (e.g. element j and i). Then, the stoichiometric coefficient of this process is written as

$$\begin{array}{ccc} \text{element 0} & \text{element } i & \text{element } j \\ \Downarrow & \Downarrow & \Downarrow \\ (v_{0l}, v_{1l}, v_{2l}, \dots, v_{nl}) & = (-1, 0, \dots, 0, 1 - \kappa, 0, \dots, 0, \kappa, 0, \dots, 0). \end{array} \quad (47)$$

Here, κ is the volume fraction ratio of two twinned martensite lattice correspondence variants. On substitution of equation (47) into (44) and considering equation (38), we have

$$\begin{aligned} \Pi_l &= (1 - \kappa) \Xi_i + \kappa \Xi_j \\ &= \Sigma : \mathbf{E}_i^* + (\Delta hT - \Delta u) - \left[(1 - \kappa) \frac{\partial f^s}{\partial z_i} + \kappa \frac{\partial f^s}{\partial z_j} \right], \end{aligned} \quad (48)$$

where

$$\mathbf{E}_i^* = (1 - \kappa) \mathbf{E}_i^{\text{tr}} + \kappa \mathbf{E}_j^{\text{tr}} \quad (49)$$

is the phase transformation eigenstrain of the habit plane variant. Equations (48) and (49) give the explicit expressions of the thermodynamic driving force of habit plane variants in terms of the phase transformation eigenstrain of habit plane variants. Although equation (48) is similar to previous models developed based on choosing martensite habit plane variants as potential wells (e.g. [7, 9, 11, 14–16, 18, 19, 60]), it is important to point out that martensite habit plane variants are not the potential wells as observed in some shape memory alloys, where habit plane variants consist of twinned martensite

correspondence variant pairs [29–31]. This similarity also indicates that our model is robust in supporting the previous models from a more fundamental sense.

We denote the volume fraction of a habit plane variant as z_l^* to distinguish it from the lattice correspondence variant, as traditionally z_l^* was denoted as z . In the forward phase transformation process, z_l^* can also be considered as a progress variable, i.e. $\zeta_l = z_l^*$ ($\zeta_l = 0$ stands for the case of whole material being austenite, while $\zeta_l = 1$ stands for the case of whole material being type l martensite habit plane variant).

The stoichiometric coefficient in reorientation (from lattice correspondence variant i to lattice correspondence variant j) can be presented as

$$\begin{array}{ccc} \text{element } i & & \text{element } j \\ \Downarrow & & \Downarrow \\ (v_{0l}, v_{1l}, v_{2l}, \dots, v_{nl}) & = & (0, \dots, 0, -1, 0, \dots, 0, 1, 0, \dots, 0). \end{array} \quad (50)$$

Substituting equation (50) into (44) and using equation (38) gives [61]

$$\begin{aligned} \Pi_l &= \Xi_j - \Xi_i = \Sigma : (\mathbf{E}_j^{\text{tr}} - \mathbf{E}_i^{\text{tr}}) - \left(\frac{\partial f^s}{\partial z_j} - \frac{\partial f^s}{\partial z_i} \right), \\ &(i, j = 1, \dots, n, i \neq j). \end{aligned} \quad (51)$$

In this transition process, the volume fraction of martensite lattice correspondence variant j may also be taken as a progress variable. $\zeta_l = 0$ stands for the situation where the whole material is lattice correspondence variant i , and $\zeta_l = 1$ stands for the case of the whole material being lattice correspondence variant j . It can also be seen from equation (51) that the reorientation between the two adjacent martensite lattice correspondence variants is independent of temperature T .

According to equation (44), if the stoichiometric coefficients of two basic processes ζ_l and ζ_m satisfy $v_{kl} = -v_{km}$, then $\Pi_l = -\Pi_m$. Therefore, ζ_m can also be represented as $-\zeta_l$, or vice versa. It is apparent that ζ_l and ζ_m are mutual reverse processes of each other. For the process variable ζ_l , $\dot{\zeta}_l > 0$ is the forward process, while $\dot{\zeta}_l < 0$ is the reverse process. Similarly, $\dot{z}_l^* > 0$ stands for the forward transformation process, and $\dot{z}_l^* < 0$ for reverse transformation process. Reorientation from the lattice correspondence variant j to the lattice correspondence variant i may be considered as a reverse process of the reorientation from the lattice correspondence variant i into the lattice correspondence variant j .

Supposing the number of martensite habit plane variants is H , there will be a total of $2H$ processes (i.e. H forward transformation processes and H reverse transformation processes). Because there are $n(n-1)$ reorientation processes among n martensite lattice correspondence variants, the total number of basic transformation process is given by

$$M_0 = 2H + n(n-1). \quad (52)$$

Otherwise the total number of basic transformation process will be $H + \frac{n(n-1)}{2}$ if two mutual reverse processes are considered as one independent process. In the present paper we take two mutual reverse processes as two processes, so that

for each basic process we always have $\dot{\zeta}_l \geq 0$. Any complex transformation process can be considered as a combination of basic transition processes. The variation of volume fractions of martensite lattice correspondence variants can be expressed in terms of the variation of M_0 basic progress variables $\dot{\zeta}_l$ ($l = 1, 2, \dots, M_0$),

$$\dot{z}_k = \sum_{l=1}^{M_0} v_{kl} \dot{\zeta}_l \quad (k = 0, 1, 2 \dots n). \quad (53)$$

For a given process, not all basic processes are involved (or in action). If basic process l is inactive, its variation is 0, i.e., $\dot{\zeta}_l = 0$.

After substituting equation (53) into (40) and considering equation (44), the second law of thermodynamics can be expressed as [61]

$$\rho T \eta^* = \sum_{l=1}^{M_0} \Pi_l \dot{\zeta}_l - \frac{1}{T} \mathbf{q} \cdot \nabla T \geq 0. \quad (54)$$

The strong form of equation (54) may be given as

$$-\frac{1}{T} \mathbf{q} \cdot \nabla T \geq 0, \quad (55)$$

and

$$\Pi_l \dot{\zeta}_l \geq 0. \quad (56)$$

3.2. Transition law

Transition laws of these M_0 basic transformation processes are considered in this section. According to the experimental results in [50], the critical condition for starting a phase transformation is

$$\Pi_l = \Pi_l^{\pm}, \quad (l = 1, 2, \dots, H), \quad (57)$$

where '+' stands for the forward transformation, and '-' for the reverse transformation. $\Pi_l^+ > 0$ and $\Pi_l^- < 0$ correspond to the critical thermodynamic driving forces for the start of the forward transformation and the reverse transformation, respectively.

The variation of volume fraction of a martensite habit plane variant is proportional to the variation of its thermodynamic driving force during a forward or reverse phase transformation [49, 50]. Thus, the phase transformation evolution equation can be expressed as

$$\begin{aligned} 2\left(\lambda + \mu \frac{1}{z_0}\right) \dot{z}_l^* &= \dot{\Pi}_l^{c+} = \dot{\Pi}_l \quad (\text{forward transformation}) \\ 2\left(\lambda + \mu \frac{1}{z_l^*}\right) \dot{z}_l^* &= \dot{\Pi}_l^{c-} = \dot{\Pi}_l \quad (\text{reverse transformation}). \end{aligned} \quad (58)$$

Here, λ and μ are non-negative material constants. λ is employed to illustrate the linear hardening phenomenon during the transformation process (i.e. the slope of lines BE, HI and FG in figure 2 is 2λ); μ is introduced to describe the nonlinear hardening behavior when the transformation approaches its end (i.e. $z_0 \rightarrow 0$ or $z_l^* \rightarrow 0$). In the forward transformation, Π_l^{c+}

increases with the thermodynamic driving force Π_l ; while in the reverse transformation, Π_l^{c-} decreases with the decrease of thermodynamic driving force Π_l . Once nucleation starts in the forward transformation, Π_l^{c-} moves back to the maximum value (Π_0^-) instantly. On the other hand, when the reverse transformation starts, Π_l^{c+} returns to the minimum value (Π_0^+). Π_0^+ and Π_0^- are materials constant with $\Pi_0^+ > 0$ and $\Pi_0^- < 0$. In most cases, $\Pi_0^+ = -\Pi_0^- = \Pi_0$.

Shown in figure 2, lines l_1 , l_0 and l_2 correspond to the cases where $\Pi = \Pi_0$, $\Pi = 0$ and $\Pi = -\Pi_0$, respectively. The size of the hysteresis loop depends not only on the distance between l_1 and l_2 (i.e., the magnitude of Π_0), but also on the slope of l_0 (i.e., $2A$, as also defined by equation (29)). The parameter Π_0 stands for the internal friction in the phase transformation, while A represents the elastic energy stored in the interphase between martensite and austenite. L'excellent [19] and others neglected the stored energy and took $A = 0$. Thus, the internal friction is the only cause of hysteresis in phase transformation. On the other hand, Huo and Müller [50] considered $\Pi_0 = 0$, i.e., the hysteresis is due to the interphase elastic energy only. In such a case, the lines l_1 , l_0 and l_2 in figure 2 coincide. It is also worth mentioning that for a material with apparent hardening behavior, the following relation holds (see also figure 2 and compare the slopes of line BE and l_0):

$$\lambda > A. \quad (59)$$

Referring to equation (58), in the forward transformation ($\dot{z}_l^* > 0$), one has

$$\Pi_l \dot{z}_l^* = \frac{z_0}{2(\lambda z_0 + \mu)} \Pi_l \dot{\Pi}_l = \frac{z_0}{4(\lambda z_0 + \mu)} \frac{d}{dt} (\Pi_l^{c+})^2 \geq 0. \quad (60)$$

In the reverse transformation ($\dot{z}_l^* < 0$)

$$\Pi_l \dot{z}_l^* = \frac{z_l^*}{2(\lambda z_l^* + \mu)} \Pi_l \dot{\Pi}_l = \frac{z_l^*}{4(\lambda z_l^* + \mu)} \frac{d}{dt} (\Pi_l^{c-})^2 \geq 0. \quad (61)$$

Thus, equation (56) can always be satisfied.

The critical condition for starting reorientation can be expressed by

$$\Pi_l = \Pi_l^{\pm}, \quad (62)$$

where '+' denotes the forward progress ($\dot{\zeta}_l > 0$), and '-' the reverse progress ($\dot{\zeta}_l < 0$), and $\Pi_l^+ > 0$, $\Pi_l^- < 0$.

Therefore the evolution equation for the reorientation process is

$$\begin{aligned} \dot{\Pi}_l &= \dot{\Pi}_l^{c+} = \lambda_1 \dot{\zeta}_l, & \text{when } \dot{\zeta}_l > 0 \\ \dot{\Pi}_l &= \dot{\Pi}_l^{c-} = \lambda_1 \dot{\zeta}_l, & \text{when } \dot{\zeta}_l < 0. \end{aligned} \quad (63)$$

Here, the variation rate of the progress variable is also assumed to be proportional to the variation of the thermodynamic driving force. λ_1 is a material constant with a positive sign. If $\dot{\Pi}_l^{c+} > 0$, $\dot{\zeta}_l > 0$; if $\dot{\Pi}_l^{c-} < 0$, $\dot{\zeta}_l < 0$. Once the forward process starts, Π_l^{c-} moves back to its maximum value (Π_{Re}^-), where the subscript Re stands for reorientation. When the reverse process starts, Π_l^{c+} returns back to its minimum value (Π_{Re}^+). Here, Π_{Re}^+ and Π_{Re}^- are material constants. Note that $\Pi_{\text{Re}}^+ \geq 0$ and $\Pi_{\text{Re}}^- \leq 0$. In most cases, $\Pi_{\text{Re}}^+ = -\Pi_{\text{Re}}^- = \Pi_{\text{Re}}^0$.

Referring to equation (63), in the forward process ($\dot{\zeta}_l > 0$)

$$\Pi_l \dot{\zeta}_l = \frac{1}{\lambda_1} \Pi_l \dot{\Pi}_l = \frac{1}{2\lambda_1} \frac{d}{dt} (\Pi_l^{c+})^2 \geq 0; \quad (64)$$

in the reverse process ($\dot{\zeta}_l < 0$)

$$\Pi_l \dot{\zeta}_l = \frac{1}{\lambda_1} \Pi_l \dot{\Pi}_l = \frac{1}{2\lambda_1} \frac{d}{dt} (\Pi_l^{c-})^2 \geq 0. \quad (65)$$

Again, equation (56) is always satisfied.

Equations (29), (36), (38), (44), (57), (58), (62) and (63) are the basic governing equations for the phase transformation and reorientation in shape memory alloys.

4. Conclusions

A constitutive model for stress-induced phase transformation and reorientation in shape memory alloy single crystal is developed. This is the first time that both forward (reverse) phase transformation and reorientation are modeled under the same thermodynamic framework. Based on the principles of thermodynamics and the ensemble average method of micro-mechanics, the macroscopic Gibbs free energy is expressed as a function of the volume fractions of different martensite lattice correspondence variants (instead of habit plane variants); those variants are chosen as the internal variables to describe the microstructure configuration of shape memory alloys. Thermodynamic driving forces corresponding to the forward/reverse phase transformation and reorientation are derived from the macroscopic Gibbs free energy.

The total elastic strain energy includes two parts: the elastic strain energy caused by the applied external load in the absence of phase transformation eigenstrain, and the interaction energy induced by the internal stress. The internal stress comes from the phase transformation eigenstrain in the absence of external load. The second part is not directly dependent on the applied external load, but indirectly on the volume fractions of martensite lattice correspondence variants.

Mori–Tanaka average theory for randomly distributed two-phase mixture is extended to the $(n + 1)$ -component mixture to evaluate the interaction energy in the phase transformation. The interaction energy is expressed as a second-order polynomial function in terms of the volume fractions of the martensite lattice correspondence variants. The total number of independent material constants in the interaction energy is no more than the number of martensite lattice correspondence variants.

The critical condition and the evolution equation for the forward/reverse phase transformation and reorientation are obtained. It is proposed to describe the complex interior hysteresis loop by a critical thermodynamic driving force jump when the opposite transition takes place.

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